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**BRIEF COMMUNICATIONS**

# Production of Nickel Sulfate Single Crystals in Processing of Nickel Oxide Electrodes of Alkaline Batteries

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**Abstract**—[$NiSO_4(H_2O)_n$] single crystals were grown by slow cooling and evaporation of a solution for sulfuric acid leaching of the active paste of a nickel oxide electrode from a spent alkaline battery. The crystals were studied by X-ray phase analysis in two measurement configurations (transmission and Bragg–Brentano focusing).

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In view of the inevitable exhaustion of natural resources, a steadily increasing fraction of the raw materials base on the market of manufacture and consumption of nonferrous metals is constituted by secondary raw materials. This can attributed in full to the battery industry. In the world practice, the ratio between the industrial applications of acid and alkaline batteries is 4 : 1, whereas in CIS countries, this ratio is 2 : 1 because of the specific technological equipment in the industry and the transportation infrastructure [1]. Alkaline nickel-iron and nickel-cadmium batteries contain large amounts of metals, such as nickel, cadmium, and copper.

As the main source of secondary nickel serve nickel oxide electrodes (NOEs) whose active paste contains 38.7– 39.1 wt % nickel [2].

Several technological schemes for processing of worked-out alkaline batteries have been described in the literature [3–5]. All these schemes include the following procedures: dismantling of a battery, separation of plates by chemical composition, leaching, and manufacture of the final product, nickel(II) hydroxide. These techniques, as a rule, differ in that a number of additional technological procedures are performed to provide a more complete recovery of the target component in the course of leaching: thermal treatment of the active paste and preliminary separation of carbon by flotation.

There exist two fundamentally different leaching methods: acid-type (sulfuric acid leaching as a particular case) and ammonia-type whose application does not require any preliminary separation of the active paste from lamels. However, a large amount of return solutions is formed in the latter case because of the poor solubility of nickel ammoniates in water. Moreover, the ammonia leaching requires a hermetically sealed apparatus because the ammonia pressure at leaching temperatures is high. With the above factors taken into account, a conclusion can be made that the efficiency of sulfuric acid leaching is higher.

A number of crystal hydrates with different amounts of water exist in the $NiSO_4$–$H_2O$ system at temperatures in the range from 269.6 to 363 K. According to published data [6], the following phases are stable: morenosite $NiSO_4 \cdot 7H_2O$ (rhombic), retgersite $\alpha$-$NiSO_4 \cdot 6H_2O$ (tetragonal), nickel hexahydrite $\beta$-$NiSO_4 \cdot 6H_2O$ (monoclinic), $NiSO_4 \cdot 2H_2O$, and dwornikite $NiSO_4 \cdot H_2O$; $NiSO_4 \cdot nH_2O$ ($n$ = 3–5) is metastable.

The crystallization of nickel sulfate from solutions containing sulfuric acid, i.e., in the $NiSO_4$–$H_2SO_4$–$H_2O$ system, has been studied at temperatures of 283–353 K [7–10].

Nickel sulfate heptahydrate crystallizes at 283 K up to a sulfuric acid content of 38.7 wt % in a saturated solution. At 293, the threshold content of sulfuric acid

decreases to 20.2 wt %. The existence range of nickel sulfate hexahydrate in the $NiSO_4$–$H_2SO_4$–$H_2O$ system corresponds to sulfuric acid concentrations in solution in the range 38.7–48.6 wt % at 283 K and 20.2–46.2 wt % at 293 K [8].

## EXPERIMENTAL

As a basis of the technological process was taken the technique for secondary processing of nickel-iron batteries, reported in [11]. One of key procedures in this technique is leaching of the active paste with $H_2SO_3$ solution with a concentration of 200–300 g $l^{-1}$ (17–26 wt %).

After dismantling worked-out alkaline batteries (nickel-iron, nickel-cadmium), we manually separated the active paste of NOEs from lamels. Then, the active paste was subjected to sulfuric acid leaching in a thermostated reactor at elevated temperatures (75–80°C). The expenditure of the acid was calculated so as to obtain a nearly saturated nickel sulfate solution.

After the leaching process was complete, carbon contained in the active paste of NOEs was separated from the solution by filtering at elevated temperatures. Then the solution was gradually cooled to the ambient temperature in an open crystallizer and then allowed to stay for several days.

In the course of cooling, we created a supersaturation sufficient for $[NiSO_4(H_2O)_n]$ crystals to formed and grow. This occurred both because the temperature was lowered to 293 K and the solution concentration increased via evaporation of the solvent. As a result, green–light blue $[NiSO_4(H_2O)_n]$ crystals with various sizes (up to 5–7 mm) were formed.

According to the solubility isotherms in the system $NiSO_4$–$H_2SO_4$–$H_2O$ at 283 and 293 K [8], the value of $n$ must be six in the given case.

We analyzed the phase composition of crystalline nickel sulfate on a STADI-P diffractometer with a mini-PSD position-sensitive detector (STOE, Germany) in two measurement configurations: in transmission ($K_{Cu\alpha 1}$) and with Bragg–Brentano focusing ($K_{Cu\alpha 1+\alpha 2}$). The measurements were made at angles in the range $2\theta$ = 5–80° with a step of 0.02°and an accumulation time of 10 s per point. Analysis of the X-ray diffraction patterns in Figs. 1 and 2, obtained in these two configurations, makes it possible to calculate the crystallographic parameters of the substance under study and to find (if any) impurity phases.

According to the results of our X-ray phase analysis, the crystals obtained in processing of NOEs of a worked-out alkaline battery are single crystals of nickel sulfate α-hexahydrate (retgersite) with a tetragonal crystal lattice. The crystallographic parameters calculated from the XPA data are listed in the table. The intensity of the characteristic lines in the diffraction pattern obtained with Bragg–Brentano focusing (Fig. 1) is substantially lower than that in the diffraction pattern measured with direct transmission of X-rays (Fig. 2).

The average values of the crystallographic parameters of crystals obtained in processing of NOEs from worked-out nickel-iron batteries, found in two measurement configurations are the following (Å): $a$ = 6.7836 ± 0.0005, $c$ = 18.2820 ± 0.0022 (transmission); $a$ = 6.7950 ± 0.0032, $c$ = 18.2919 ± 0.0118 (Bragg–

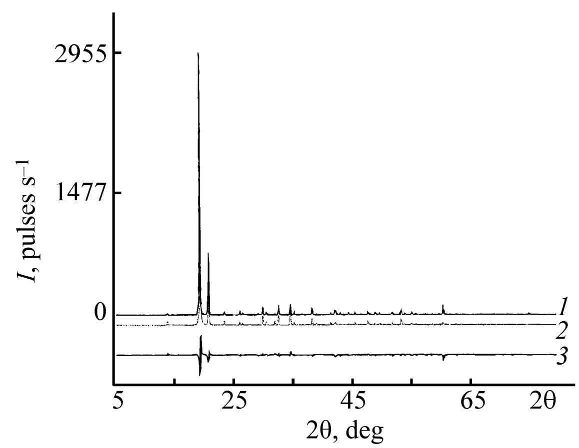


**Fig. 1.** X-ray diffraction pattern of a $[\alpha\text{-}NiSO_4(H_2O)_6]$ crystal, measured with Bragg–Brentano focusing ($K_{Cu\alpha 1+\alpha 2}$). (*I*) Radiation intensity and ($2\theta$) Bragg angle: the same for Fig. 2. (*1*) $I_{exp}$, (*2*) $I_{calc}$, and (*3*) $I_{exp} - I_{calc}$; the same for Fig. 2.

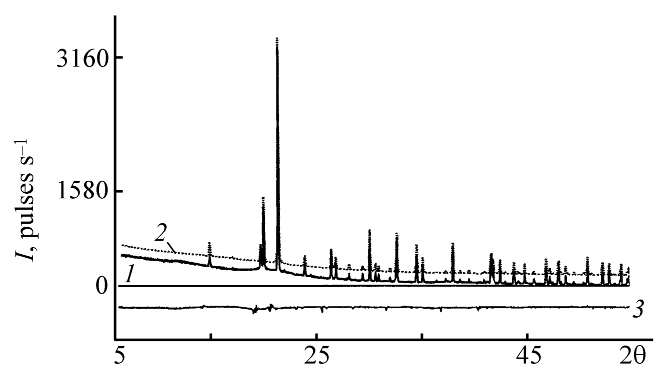


**Fig. 2.** X-ray diffraction pattern of a $[\alpha\text{-}NiSO_4(H_2O)_6]$ crystal, measured in transmission of X-rays ($K_{Cu\alpha 1}$).

Crystallographic parameters of [$\alpha$-$NiSO_4(H_2O)_6$] obtained in processing of nickel oxide electrodes of worked-out nickel-iron batteries

| Transmission | | | Bragg–Brentano focusing | | |
|---|---|---|---|---|---|
| *a*, Å | *c*, Å | *V*, Å$^3$ | *a*, Å | *c*, Å | *V*, Å$^3$ |
| 6.782(2) | 18.281(6) | 842.90 | 6.783(4) | 18.26(1) | 841.00 |
| 6.784(2) | 18.288(6) | 842.90 | 6.792(4) | 18.29(1) | 841.70 |
| 6.784(2) | 18.278(6) | 843.60 | 6.794(4) | 18.27(1) | 843.80 |
| 6.783(2) | 18.279(6) | 842.90 | 6.794(4) | 18.31(1) | 841.00 |
| 6.783(2) | 18.280(6) | 841.00 | 6.799(4) | 18.32(1) | 844.90 |
| 6.784(2) | 18.283(6) | 840.90 | 6.801(4) | 18.31(1) | 841.50 |
| 6.783(2) | 18.282(6) | 842.90 | 6.793(4) | 18.29(1) | 840.90 |
| 6.783(2) | 18.279(6) | 841.20 | 6.798(4) | 18.29(1) | 843.90 |
| 6.784(2) | 18.282(6) | 842.90 | 6.796(4) | 18.29(1) | 841.40 |
| 6.785(2) | 18.286(6) | 842.90 | 6.795(4) | 18.29(1) | 841.00 |
| 6.783(2) | 18.278(6) | 841.70 | 6.796(4) | 18.28(1) | 844.40 |

Brentano focusing). The results obtained by measuring X-ray diffraction patterns in different ways are well consistent.

The lattice constants of retgersite [$\alpha$-$NiSO_4(H_2O)_6$], reported in [12], are $a = 6.785(2)$ Å and $c = 18.288(3)$ Å, in good agreement with our experimental data.

A comparison of theoretically calculated diffraction patterns with those obtained experimentally demonstrated that the crystalline [$\alpha$-$NiSO_4(H_2O)_6$] obtained in the study is X-ray-pure and can be used in industries requiring reagent-pure nickel sulfite.

## CONCLUSIONS

(1) Single-crystal [$\alpha$-$NiSO_4(H_2O)_6$] was obtained in processing of nickel oxide electrodes of worked-out alkaline electrodes.

(2) The crystallographic parameters of nickel sulfate $\alpha$-hexahydrate (retgersite), found by X-ray diffraction analysis in two measurement configurations are the following (Å): $a = 6.7836 \pm 0.0005$, $c = 18.2820 \pm 0.0022$ (transmission); $a = 6.7950 \pm 0.0032$, $c = 18.2919 \pm 0.0118$ (Bragg–Brentano focusing).

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